Petroleum HPV

201-15837

March 16, 2005

Administrator
U.S. Environmental Protection Agency
P.O. Box 1473
Merrifield, VA 22116
Attention: Chemical Right-to-Know Program

HPV Challenge Program, AR-201
HPV Consortium #

Re: Response to Comments on the Reclaimed Substances Test Plan

Dear Administrator:

The Petroleum HPV Testing Group (Testing Group) is a consortium representing 92 percent of the nation's petroleum refining capacity. The Testing Group is made up of 60 member companies of the American Petroleum Institute (API), the National Petrochemical & Refiners Association (NPRA), the Gas Producers Association (GPA) and the Asphalt Institute. The Testing Group appreciates the comments it received on its Test Plan for Reclaimed Substances that was posted to the Agency's ChemRTK website on January 20, 2004.

The Environmental Protection Agency (EPA), The National Cancer Institute (NCI), Environmental Defense and the People for the Ethical Treatment of Animals (on behalf of several animal welfare organizations) submitted comments on the Test Plan. In the interest of communicating our intent with all interested stakeholders, the Testing Group is providing a single response to all of the comments received. We will also be providing a revised test plan and robust summary for posting on the ChemRTK website. The revised documents will also be posted on the Testing Group's website at www.petroleumhpv.org after the comments have been incorporated.

General Comments

The Testing Group included four separate, distinct categories of substances in the test plan for Reclaimed Substances. This caused considerable confusion among the reviewers as several of them perceived that the four categories were somehow chemically related. That is not the case. The Testing Group chose to address all four separate categories in a single test plan although only one of the categories (naphthenic acids) was actually being evaluated for SIDS data adequacy. The other three categories, for the reasons stated in the plan, were not evaluated for data adequacy and no testing was proposed. To avoid further confusion, the Testing Group is revising the test plan to include only the "naphthenic acids"category. **The test plan will be renamed "Reclaimed Substances: Naphthenic Acids".** The HPV status of the other three categories (phenols, disulfides, and acids/bases) will be addressed in technical letters to the Agency.

Comment: One reviewer disagreed with the Testing Group's contention that these materials should be exempt from testing because they are not released, transported or used in such a manner that might present a threat to human or environmental health.

Response: The Testing Group is in the process of providing documentation to EPA substantiating that many of the materials in the phenolic and disulfide categories should be considered "no longer HPV". With respect to the highly alkaline or acidic streams, we are in agreement with comments received from EPA which indicated that "testing members of this category is unnecessary as their toxicological effects will reflect their extreme pH values and corrosivity".

Category Definition

Comment: No representative chemical structures for naphthenic acids were included.

Response: The revised test plan will include a more comprehensive description of the petroleum-derived naphthenic acids that are refined and sold commercially. Chemical structures of typical naphthenic acids found in these streams will be provided, and the specific carbon ranges of the naphthenic acids provided. In practice, naphthenic acids are obtained largely from straight run middle distillate streams (diesel and kerosene). Consequently, typical commercial naphthenic acids consist of carboxylic acids with carbon numbers ranging between C10 and 22. The actual chemical species present in these mixtures varies with the source of the parent crude oil and are not well characterized, since product specifications include properties such as acid number (number of mg KOH that react per g of sample), unsaponifiable content, and color, rather than chemical composition.

Category Justification

Comment: No information was presented in the test plan about the potential impact of differences in composition on health or environmental effects.

Response: The Testing Group assumes that naphthenic acids, as a group, will have similar health and environmental effects. As indicated in our test plan, the term naphthenic acid, as commonly used in the petroleum industry, refers collectively to all of the carboxylic acids present in crude oil. The actual chemical species present in these mixtures varies with the source of the parent crude oil and are not well characterized, since product specifications include properties such as acid number (number of mg KOH that react per gram of sample), unsaponifiable content, and color, rather than chemical composition. Because of the diversity of chemical species present in these mixtures, it would be very difficult to design studies to correlate chemical composition with specific health or environmental endpoints.

Test Plan – Fate and Environmental Effects

Comment: Estimated water solubility values ranged from 0.002 mg/L for a 2-ring cyclohexane to 2.1 mg/L for a 4-ring cyclohexane. The submitter needs to address the 1000-fold difference for chemicals with nearly identical molecular weights.

Response: The revised robust summary and test plan will include changes and/or explanations addressing water solubility values for representative constituents in naphthenic acid mixtures.

Comment: In the Biodegradation section, the submitter needs to explain why all of the tested single compounds, which have the carboxyl group attached directly to the ring, are considered representative when, according to the test plan "the carboxyl group is usually attached to a side chain rather than directly to the ring".

Response: Neither the Test Plan nor robust summary information state that compounds in which the carboxyl group is attached directly to the naphthenic ring are representative of all naphthenic acids. The robust summary Section 3.8 does include biodegradation data on such compounds, but it also includes data on complex mixtures of naphthenic acids. The reviewer is referred to the study by Herman, et al. (1994), which is summarized in Section 3.8 of the Robust Summary. That study included biodegradation of single compounds, natural mixtures of naphthenic acids extracted from oil sands tailings, and a commercially-available sodium naphthenate mixture, the latter two existing as highly complex mixtures of different molecular weight naphthenic acids. The Testing Group assumes these complex naphthenic acid mixtures will contain both types of materials, ones in which the carboxyl group is attached directly to the naphthenic ring and ones in which the carboxyl group is attached to a side chain.

Comment: The submitter did not specifically address fugacity for the sodium naphthenate intermediate stream. The salts are likely to have greater mobility in the environment because of their increased water solubility and higher partitioning to water.

Response: The Testing Group has subsequently determined that "naphthenic acids, sodium salts", CASRN 61790-13-4, was improperly reported by the only manufacturer who sponsored the material. The Testing Group intends to desponsor the material in separate correspondence to the Agency. Therefore, no additional information is required for the test plan.

Test Plan - Health Effects

Comment: EPA indicated that the NTP *in vitro* data provided for sodium naphthenate are inadequate because no data summaries were provided.

Response: The test plan is being revised to include a bacterial mutagenicity assay on a naphthenic acid sample. Subsequent to submitting the test plan, the Testing Group has obtained detailed summaries of the NTP assays. After reviewing these summaries, the Testing Group has determined that the data are not relevant because the test material used by NTP is not similar to naphthenic acid mixtures derived from petroleum streams. An in-vivo mutagenicity component is already part of the proposed repeat dose/reproductive/developmental toxicity screen.

Comment: Several reviewers indicated that the existing database for naphthenic acids is adequate and indicated that the submitter should make use of available data prior to having these studies repeated.

Response: The test plan evaluated the all available toxicity studies of naphthenic acids, which included acute, repeat-dose, dermal application, and developmental toxicity studies. Most of the studies cited by the reviewers were evaluated. Some did not meet OECD guidelines for reasons described in the test plan, and some were incorporated into the data summary. While referred to by several reviewers, no NTP carcinogenicity study exists. The Testing Group confirmed the lack of these studies by contacting NTP. Comments received from NCI confirm the Testing Group's assessment, i.e. that additional studies are necessary to adequately characterize the hazard of naphthenic acids.

As regards the adequacy of the two developmental studies cited in the Robust Summaries:

- The one-generation reproduction study on calcium naphthenate was obtained from EPA and reviewed. The Testing Group continues to maintain that the study is adequate for

supplementation purposes only. The applicability of results on the calcium naphthenate substance used in this study to commercial naphthenic acids derived from petroleum streams is questionable. The study design is also inadequate in certain respects, e.g. female animals were not treated with test material. The robust summary will be updated to include more details and to indicate why the Testing Group considers the study inadequate.

- The developmental toxicity study on naphthenic acids obtained from Athabasca tar sand extraction was reported in 2002 in abstract form and has not been published in full. The Testing Group has been unable to obtain more complete documentation of the study details to determine whether it meets OECD guideline criteria. In addition, it is not known how representative Athabasca tar sands may be of the commercial, petroleum-derived naphthenic acids.

Robust Summaries

Comment: The robust summaries did not identify or assign CAS numbers to the test materials.

Response: The Testing Group will determine whether CAS number information is available for the studies cited and update the robust summaries accordingly.

Closing Remarks

The Testing Group appreciates the comments of EPA, ED, PETA and NCI, as well as their interest in the test plan for Naphthenic Acids. We believe that the revised test plan, being submitted under separate cover, is both scientifically sound and meets the intent of the HPV testing program as well as EPA's guidance on animal welfare.

If you have further questions about these substances, please don't hesitate to contact me at (202) 682-8344.

Sincerely,

Lorraine Twerdok, Ph.D., DABT
Program Manager
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